

VARIABILITY OF OPTICAL ATTENUATION AND FLUORESCENCE IN COASTAL ENVIRONMENTS

Dr. Rod G. Zika
University of Miami
Rosenstiel School of Marine and Atmospheric Science
Division of Marine and Atmospheric Chemistry
4600 Rickenbacker Causeway
Miami, Florida 33149
rzika@rsmas.miami.edu
Phone (305)361-4715
Fax (305) 361-4689

Award # N000149510207

LONG-TERM GOALS

Our primary long-term scientific goal in this program has been to develop an understanding of the physical and chemical processes affecting CDOM (colored dissolved organic matter) and the resultant changes of attenuation of ultraviolet and visible radiation in seawater. The chemical constituent of seawater which absorbs most of the incident solar radiation is collectively referred to as colored dissolved organic matter (CDOM). CDOM is a complex aggregate of various organic compounds derived from marine and terrestrial origins. The two major sources of the CDOM are the marine biota (e.g. exudates and recycling products) and terrestrial humic material which is introduced to the oceans mainly by rivers. It is the photochemically active fraction of these two major sources that initiate most of the photochemical reactions in seawater. Such reactions not only alter the CDOM, but also initiate reaction chains which affect the chemical speciation of oxygen, transition metals, and various organic compounds. These reactions can have profound effects on the chemical characteristics of seawater and also on biological and physical properties such as optical absorbance and luminescence.

OBJECTIVES

The emphasis in this program has been placed on the study of the factors affecting the optical characteristics of seawater. Particular emphasis has been placed on developing a better understanding of the differences and similarities between CDOM of marine and terrestrial origin and the impact these properties have on the chemical and optical characteristics of coastal environments, where the effects are most pronounced. There were two principal objectives during the past year: the first was to commence the development of a new method involving the application of Flow Field Flow Fractionation (FFFF) to characterize the optical properties of coastal CDOM, and the second was to complete and disseminate the results of two graduate student studies on the photochemical formation of various low molecular weight gases from DOM. This work is supported by ONR Biological Oceanography and Ocean Optics.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 30 SEP 1997		2. REPORT TYPE		3. DATES COVERED 00-00-1997 to 00-00-1997	
4. TITLE AND SUBTITLE Variability of Optical Attenuation and Fluorescence in Coastal Environments				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Miami,Rosensteil School of Marine and Atmospheric Science,4600 Rickenbacker Causeway,Miami,FL,33149				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 4	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

APPROACH

A combination of short cruises to local coastal environments around South Florida coupled with intensive post-cruise laboratory experiments have been the principal mode of operation during the last year. The cruises were used to obtain samples for return to the laboratory and to characterize the environment from which the samples were obtained by measuring a variety of optical, chemical, biological, and physical properties. With the availability of the FFFF during the latter part of the year more time was devoted to developing and utilizing this technology.

WORK COMPLETED

As the result of a DURIP award for this year the components for a FFFF system have been purchased and assembled. That system is now operational and method development for the characterization of CDOM is currently underway. A coastal cruise aboard the R. V. Calanus was successfully conducted during the last year to provide samples for the FFFF system and field data for two Ph.D. dissertations. One of the students successfully defended his dissertation (Pos, W. H. 1997a) earlier this year and the other is scheduled to defend in December of this year. Papers were presented at the San Francisco AGU meeting and the Santa Fe ASLO meeting in early 1997. During the last year we have 4 published or in press papers related to our ONR work and 5 presentations.

RESULTS

Early results from the application of the technique of FFFF for the characterization of colored dissolved organic matter (CDOM) samples indicate that very different results are obtained when compared to other more traditional separation techniques (e.g. gel permeation chromatography). Work is underway to determine optimal separation conditions and to establish procedures for producing detailed optical characterization of the fractionated CDOM from various environments. Both optical absorption and fluorescence properties are being measured. This should prove to be a novel and very useful technique for understanding the complex optical properties of aquatic CDOM.

Studies on the volatile photochemical breakdown products of DOM (i.e. CO, CO₂, COS and hydrocarbons) have been completed and will appear in two Ph.D. dissertations (Pos, W. H. ,1997a and Riemer, D. 1997). The details of these results are being disseminated in the literature and in national meeting presentations (Pos et al., 1997b, c,d,e; Pos et al. 1996; Riemer et al., 1997; Riemer et al., 1996; Zika et al., 1997). Of particular interest is the observation that substantial amounts of CO₂ are photochemically generated from DOM in coastal environments (Pos et al., 1997c).

IMPACT

Aside from developing an understanding of chemistry and physics of light in the ocean there are other more applied goals. The most important of these is the development of new analytical techniques and processing capabilities which provide for high frequency sampling with near real time data acquisition and data processing. This has been accomplished through the development of computer applications that involve interfacing various simultaneous data channels into a shipboard network, including in-the-water sampling micro-processors, and ship laboratory computers (which process and display the incoming data).

TRANSITIONS

The results from this work and other related studies show that our understanding of CDOM and its effects on the optical properties of the ocean and particularly coastal ocean are marginal. The lack of such information dramatically limits the application of strategic approaches to remote and in situ observational methods such as satellites or submerged detection systems. Understanding the chemical and physical characteristics of the CDOM is essential for the development of accurate optical methods and modeling tools. This is particularly true for coastal environments.

RELATED PROJECTS

The cruise during the last year involved ONR funded investigators from optical physics, marine biology and marine chemistry. A thorough understanding of the nature of CDOM in the oceans requires a multi-disciplinary approach. Future endeavors should also include the area of remote sensing.

REFERENCES

Pos, W. H., D. D. Riemer and R. G. Zika. "Photoproduction of Carbon Monoxide and Carbonyl Sulfide in Seawater: Laboratory Indications of a Coupled Production Pathway". AGU Fall Meeting, Dec. 15-19 1996, San Francisco CA.. Trans. Am. Geophys. U., 77: 42E-01, F280 (Poster).

Pos, W. H. On the Processes and Mechanisms effecting Carbonyl sulfide and Carbon monoxide Photoproduction in Natural Waters. Ph. D. dissertation, Georgia Institute of Technology . 1997a

Pos, W. H., P. J. Milne, D. D. Riemer and R. G. Zika. Photoinduced oxidation of H₂S species: A sink for sulfide in seawater. J. Geophys. Res. 102(D11): 12831-12837 1997b

Pos, W. H., P. J. Milne, D. D. Riemer and R. G. Zika. Photoproduction of carbonyl sulfide, carbon monoxide and carbon dioxide in the West Coastal waters of Florida: A photochemical study of plumes. (JGR, in press) 1997c

Pos, W., D. Riemer and R. Zika. "CO and OCS Photoproduction in seawater: Evidence for a coupled photoproduction pathway." ASLO 97 Aquatic Sciences Meeting, Feb. 10-14 1997, Santa Fe NM. 1997d.

Pos, Willer H., D. D. Riemer and Rod Zika. Carbonyl Sulfide (OCS) and Carbon Monoxide (CO) in natural waters: Evidence of a coupled photoproduction pathway. Marine Chemistry (accepted) 1997e.

Riemer, D. D., W. H. Pos, and R. G. Zika. "Photochemical Production of Non-Methane Hydrocarbons (NMHCs) in Seawater A Process involving Dissolved Organic Matter (DOM)". AGU Fall Meeting, Dec. 15-19 1996, San Francisco CA.. Trans. Am. Geophys. U., 77: H32C-01, F256 (Poster).

Riemer, D. D., W. H. Pos, and R. Zika. 1997. "Nonmethane Hydrocarbons (NMHCs) in Seawater: Photochemical Production from Dissolved Organic Matter (DOM)". ASLO 97 Aquatic Sciences Meeting, Feb. 10-14 1997, Santa Fe NM. (Poster)

Zika, R., W. Pos, D. Riemer, F. Millero, C. Moore and C. Farmer. 1997. "Photoproduction of Carbonyl Sulfide, Carbon Monoxide, and Carbon Dioxide in the West Coastal Waters of Florida". ASLO 97 Aquatic Sciences Meeting, Feb. 10-14 1997, Santa Fe NM. (Poster)